Formulation and implementation of a relativistic unrestricted coupled-cluster method including noniterative connected triples

Visscher, L.; Lee, T. J.; Dyall, K. G.

Published in:
Journal of Chemical Physics

DOI:
10.1063/1.472655

Formulation and implementation of a relativistic unrestricted coupled-cluster method including noniterative connected triples

Lucas Visscher, Timothy J. Lee, and Kenneth G. Dyall

Citation: The Journal of Chemical Physics **105**, 8769 (1996); doi: 10.1063/1.472655
View online: https://doi.org/10.1063/1.472655
View Table of Contents: http://aip.scitation.org/toc/jcp/105/19
Published by the American Institute of Physics

Formulation and implementation of a relativistic unrestricted coupled-cluster method including noniterative connected triples

Lucas Visscher[a)]
Laboratory of Chemical Physics and Material Science Center, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

Timothy J. Lee
NASA Ames Research Center, MS 230-3, Moffett Field, California 94035-1000

Kenneth G. Dyall
Thermosciences Institute, NASA Ames Research Center, Moffett Field, California 94035-1000

(Received 3 June 1996; accepted 14 August 1996)

The formalism for a relativistic open-shell CCSD(T) method is presented and implemented in a computer program, RELCCSD. The code can be used for calculations with 2- or 4-component relativistic reference wave functions and allows a full inclusion of the spin–orbit coupling. The code is interfaced to the MOLFDIR program system. We illustrate its use with *ab initio* calculations of the fine structure splittings of Cl, FO, ClO, O_2^+, and O_2^-. The triples correction is found to make a large contribution to the Cl atom splitting, which is within 23 cm^{-1}, of the experimental value. The molecular results are within 4 cm^{-1} of the experimental values where these are available. The value for FO is predicted to be -195 ± 4 cm^{-1}, in good agreement with experiment. © *1996 American Institute of Physics.* [S0021-9606(96)01243-3]

I. INTRODUCTION

The spin–orbital singles and doubles coupled cluster (CCSD) equations[1–4] can be used in relativistic electronic structure methods that use 2- or 4-component spinors as 1-particle basis functions. The starting point of such methods is the Dirac–Coulomb–(Breit) Hamiltonian, which is either used directly or transformed to a more convenient approximate Hamiltonian. We will not go into the details of the different methods, but assume that a set of basis spinors is found that can be identified as belonging to either the electronlike positive energy part of the spectrum, or to the positronlike negative energy part. We will work in the no-pair approximation, i.e., neglecting positron–electron pair creation, so that the second quantized Hamiltonian assumes the same form as in nonrelativistic theory,[5]

$$\hat{H}^{NP}=\sum_{P,Q} Z_Q^P \hat{E}_P^Q+\tfrac{1}{4}\sum_{P,Q,R,S} V_{RS}^{PQ}\hat{E}_{PQ}^{RS}. \tag{1}$$

In this Hamiltonian $Z_Q^P=\langle Q|h|P\rangle$ and $V_{RS}^{PQ}=\langle RS\|PQ\rangle$ represent the one-electron and antisymmetrized two-electron integrals, respectively. The $\hat{E}_P^Q$ and $\hat{E}_{PQ}^{RS}$ operators are the replacement operators as defined by Paldus.[5] In this formulation the nonrelativistic theory and various realizations of the no-pair approximation only differ in the definition of the scalar quantities Z and V.

In the nonrelativistic spin–orbital Hamiltonian the one-electron functions can be written as a product of a spatial and a spin part which means that the spin-integration can be performed separately. This is also true for the so-called spin-free relativistic approximations.[6–8] Those approximations have the advantage that one may treat electron correlation using standard methods and computer codes after a transformation to the molecular spinor basis. In cases where the spin–orbit coupling effects are large it is desirable to include the spin–orbit coupling terms as well. This can either be done by adding a spin–orbit coupling operator to the spin-free Hamiltonian, or by using an implicitly coupled Hamiltonian like the untransformed Dirac–Coulomb–(Breit) equation or the two-component zeroth order regular approximation (ZORA) equation.[9–11] In both cases one will find that additional classes of two-electron integrals have to be considered, since the spin-integration can no longer be factored out. In general the 2- or 4-component spinors ψ are now written as a sum of spin–orbitals φ in which the coefficients will assume complex values,

$$\begin{aligned}\psi_P(\mathbf{r},\eta)&=\sum_u \sum_\eta^{\alpha,\beta} c_{u,\eta}^P \varphi_u(\mathbf{r},\eta)\\ &=\sum_u \sum_\eta^{\alpha,\beta} c_{u,\eta}^P \phi_u(\mathbf{r})\sigma_\eta(\eta).\end{aligned} \tag{2}$$

Based on this relation between spinors and spin–orbitals all equations may be written in terms of spin–orbitals. In the spin–orbit (SO) configuration interaction (CI) type of approach,[12–15] for instance, the spin–orbit interaction is neglected at the Hartree–Fock and CI levels, and an effective spin–orbit operator is included afterwards to describe the coupling between CI wave functions of different symmetries.

We assume that the spin–orbit interaction is already taken into account at the Hartree–Fock level. The spinors are true eigenfunctions of a spin-dependent Fock-operator and the reference is written as a single spinor-determinant. The last constraint makes the method different from relativistic multireference approaches like the state-universal Fock space

a)Present address: Chemistry Department, Odense University, Campusvej 55, DK-5230 Odense M, Denmark.

CC method of Ilyabaev and Kaldor,[16] which has been applied to closed and open shell atoms.[17]

In a previous paper[18] we have shown that for closed-shell molecules that possess at least one twofold element of symmetry, one can use a Kramers-restricted method to make optimal use of the existing symmetry relations between the amplitudes and integrals. In this paper we present the more general, but computationally less efficient, unrestricted scheme that allows us to treat single-reference open-shell systems as well.

II. THEORY

A. The CCSD equations

The starting point is the well known spin–orbital form of the CCSD equations. We follow the formulation of Jayatilaka and Lee,[19] slightly rewritten to express all equations in terms of the antisymmetrized integrals. This formulation is already given in our previous paper[18] but for completeness we will give the equations here as well. Occupied spinors are labeled by I, J, K, L while unoccupied spinors are labeled by A, B, C, D. In the following formulae the t_1 and t_2 cluster amplitudes are represented by a capital T. The CCSD energy equation is written in the form,

$$E^{\mathrm{CCSD}}=\sum_{I,A} F_A^I T_I^A+\sum_{\substack{I<J\\A<B}} V_{AB}^{IJ}\tau_{IJ}^{AB}. \tag{3}$$

The amplitudes are determined by the equations,

$$\begin{aligned} F_I^A &- 2\sum_{K,C} F_C^K T_K^A T_I^C+\sum_C H_C^A T_I^C-\sum_K H_I^K T_K^A \\ &+\sum_{K,C} H_C^K(T_{IK}^{AC}+T_K^A T_I^C)+\sum_{K,C} V_{IC}^{AK} T_K^C \\ &+\sum_{K,C<D} V_{CD}^{AK}\tau_{IK}^{CD}-\sum_{K<L,C} V_{IC}^{KL}\tau_{KL}^{AC}=0, \end{aligned} \tag{4}$$

$$\begin{aligned} V_{IJ}^{AB} &+ P_{AB}\left(\sum_C G_C^A T_{IJ}^{CB}-\sum_K V_{IJ}^{AK} T_K^B\right)-P_{IJ}\left(\sum_K G_I^K T_{KJ}^{AB}\right. \\ &\left.-\sum_C V_{IC}^{AB} T_J^C\right)+\sum_{K<L} A_{IJ}^{KL}\tau_{KL}^{AB}+\sum_{C<D} B_{CD}^{AB}\tau_{IJ}^{CD} \\ &+ P_{IJ}P_{AB}\left(\sum_{K,C} H_{IC}^{AK} T_{JK}^{BC}-\sum_{K,C} V_{IC}^{AK} T_J^C T_K^B\right)=0, \end{aligned} \tag{5}$$

where the permutation operator P_{PQ} is used

$$P_{PQ}f(P,Q)=f(P,Q)-f(Q,P) \tag{6}$$

and the intermediates are defined as

$$F_P^Q=Z_P^Q+\sum_K V_{PK}^{QK}, \tag{7}$$

$$\tau_{IJ}^{AB}=T_{IJ}^{AB}+T_I^A T_J^B-T_J^A T_I^B, \tag{8}$$

$$H_C^A=F_C^A-\sum_{K<L,D} V_{CD}^{KL}\tau_{KL}^{AD}, \tag{9}$$

$$H_I^K=F_I^K+\sum_{L,C<D} V_{CD}^{KL}\tau_{IL}^{CD}, \tag{10}$$

$$H_C^K=F_C^K+\sum_{L,D} V_{CD}^{KL} T_L^D, \tag{11}$$

$$G_C^A=H_C^A-\sum_K F_C^K T_K^A+\sum_{K,D} V_{CD}^{AK} T_K^D, \tag{12}$$

$$G_I^K=H_I^K+\sum_C F_C^K T_I^C+\sum_{L,C} V_{IC}^{KL} T_L^C, \tag{13}$$

$$A_{IJ}^{KL}=V_{IJ}^{KL}+P_{IJ}\left(\sum_C V_{IC}^{KL} T_J^C\right)+\sum_{C<D} V_{CD}^{KL}\tau_{IJ}^{CD}, \tag{14}$$

$$B_{CD}^{AB}=V_{CD}^{AB}-P_{AB}\left(\sum_K V_{CD}^{AK} T_K^B\right), \tag{15}$$

$$\begin{aligned} H_{IC}^{AK} &= V_{IC}^{AK}+\sum_L V_{IC}^{KL} T_L^A-\sum_D V_{CD}^{AK} T_I^D \\ &+\sum_{LD} V_{CD}^{KL}\left(\frac{1}{2} T_{IL}^{AD}-T_I^D T_L^A\right). \end{aligned} \tag{16}$$

B. Perturbational triples corrections

The error made in truncating the coupled-cluster expansion of the wave function to single and double excitations of the reference can be reduced significantly by introducing a perturbative estimate of the connected triple excitations. The most popular of such schemes, CCSD(T),[20] has shown to give reliable results even in cases where the single-reference approach starts to break down.[21,22] This method includes terms up to fifth order in perturbation theory. It has an n^7 dependency on the number of orbitals, which is one order less than the full CCSDT model. Recently, Deegan and Knowles[23] published a new method, CCSD-T, that differs from CCSD(T) by an additional fifth order perturbation term. This method gives slightly better results for the test cases that they presented. We have implemented both formalisms and, since the extension is trivial, also the older CCSD+T formalism[24] that includes only fourth order terms. We write the relevant equations, following Deegan and Knowles as

$$\Delta E^{(T)}=-\sum_{I<J<K}\sum_{A<B<C} W_{ABC}^{IJK}\frac{(W_{ABC}^{IJK}-Y_{ABC}^{IJK})}{\epsilon_{ABC}^{IJK}}, \tag{17}$$

where W is defined as

$$W_{IJK}^{ABC}=P_{IJK}P_{ABC}\left(\sum_E V_{IE}^{AB} T_{JK}^{EC}+\sum_L V_{IJ}^{AL} T_{KL}^{BC}\right) \tag{18}$$

with P_{PQR} the three-index permutation operator

$$P_{PQR}f(P,Q,R)=f(P,Q,R)+f(Q,R,P)+f(R,P,Q). \tag{19}$$

Y is defined differently for the three triples corrections. In the simplest formulation, CCSD+T, Y is equal to zero. In the CCSD(T) formalism Y is defined as

$$Y_{IJK}^{ABC}=P_{IJK}P_{ABC}(V_{IJ}^{AB} T_K^C+T_{IJ}^{AB} F_K^C). \tag{20}$$

In the CCSD-T formalism Y is defined as

$$Y_{IJK}^{ABC} = P_{IJK}P_{ABC}(T_{IJ}^{AB}T_K^C + \tfrac{1}{3}\,P_{IJ}T_I^A T_J^B T_K^C)\epsilon_{IJK}^{ABC}. \quad (21)$$

ϵ_{IJK}^{ABC} is defined as the difference of spinor energies

$$\epsilon_{IJK}^{ABC} = \epsilon_I + \epsilon_J + \epsilon_K - \epsilon_A - \epsilon_B - \epsilon_C. \quad (22)$$

C. Restricted open shell zeroth order Hamiltonian

The choice of canonical or noncanonical spinors is immaterial for the form of the CCSD equations given above, since we include possible nonzero off-diagonal Fock matrix elements in the formalism. The particular choice of spinors may, of course, still influence the results. For closed shells, the obvious choice is to use canonical Hartree–Fock spinors. In this case the spinors are related by time-reversal or Kramers symmetry. This gives symmetry relations in the density matrices and 2-electron integrals that may be utilized in the Hartree–Fock self-consistent field procedure and the transformation of the integrals to a molecular spinor basis. For open shell systems one may choose to use a Kramers-restricted formalism in which both components of a Kramers pair are restricted to have the same fractional occupation. This formalism is closely related to the ROHF scheme used in nonrelativistic or scalar relativistic HF schemes. The advantage is that the same relations in the density and Fock-matrices and 2-electron integrals hold as in the closed shell case.

For the evaluation of the triples correction we need to define the zeroth order Hamiltonian used in the perturbation theory. In our formalism this is the diagonal operator

$$\hat{H}^0 = \sum_P \epsilon_P \hat{E}_P^P. \quad (23)$$

The perturbation is consequently defined as

$$\hat{H}^1 = \sum_{P,Q} U_Q^P \hat{E}_P^Q + \tfrac{1}{4} \sum_{P,Q,R,S} V_{RS}^{PQ} \hat{E}_{PQ}^{RS}. \quad (24)$$

The exact definition of H^0 and H^1 is now dependent on the choice of spinors (canonical spinors eliminate the matrix U) and the value of ϵ_P. This is of importance for the open shell case where the Fock matrix will be nondiagonal and different choices of Hartree–Fock schemes are possible.

It is important to note that ultimately the choice of H^0, H^1, and the ϵ_P quantities defines the perturbation theory that is used to construct the $+T$, (T), and $-T$ corrections for connected triple excitations. There has been considerable work over the last few years on single reference restricted open-shell perturbation theories (e.g., see Refs. 25–28, and references therein), and without going in too much detail, it has been shown that the characteristic most important for developing a rapidly convergent open-shell perturbation theory is that the orbital or spinor energies ϵ_P be different for the occupied and unoccupied open-shell spin–orbitals or spinors. For example, in the most successful nonrelativistic restricted open-shell perturbation theories these differ by an exchange integral. Most of these theories also have in common that a set of so-called semicanonical molecular orbitals is defined which leaves the Fock matrix truly diagonal in the occupied and virtual subspaces (this also has implications regarding the orbital invariance of the perturbation energies, see Ref. 29 for a detailed discussion). Other recent studies have investigated the effect of different ϵ_P choices[30] and the use of semicanonical orbitals[31] on the CCSD(T) energies from a numerical perspective. In agreement with previous studies of restricted open-shell perturbation theories, Neogrády and Urban[30] found perturbational triples corrections to be better when using diagonal Fock matrix elements F_P^P, for the ϵ_P quantities rather than orbital energies from the restricted Hartree–Fock calculation. Both recent studies found that the use of semicanonical orbitals had little effect on the perturbational triples corrections. Therefore, in the present study we choose the ϵ_P quantities to be the diagonal elements of the Fock matrix, F_P^P, and the spinors to be the Kramers-restricted open-shell Dirac–Hartree–Fock spinors.

A more rigorous approach to the open-shell problem would be to extend the open-shell Kramers-restricted formalism to the CCSD level. In such an approach one forces the amplitudes to display the same symmetry relations as are present in the integrals, similar to what Jayatilaka and Lee[32] have done for nonrelativistic restricted open-shell coupled cluster theory. This will also lead to a more efficient formalism because the number of independent amplitudes and integrals can be reduced. Since the CCSD(T) step in the present implementation takes only a fraction of the time of a complete 4-component relativistic calculation, and the accuracy of the present method is satisfactory, we have not yet explored this possibility in detail.

The CCSD code is interfaced to the MOLFDIR (Ref. 33) program system, where the spinors are obtained using different Fock operators for closed and open shells respectively.[34,35] At convergence the Fock matrices are given by

$$F_L^M = Z_L^M + \sum_K^{\text{closed}} V_{LK}^{MK} + f\sum_V^{\text{open}} V_{LV}^{MV}, \quad (25a)$$

$$F_T^U = Z_T^U + \sum_K^{\text{closed}} V_{IK}^{UK} + af\sum_V^{\text{open}} V_{TV}^{UV}, \quad (25b)$$

$$F_D^E = Z_D^E + \sum_K^{\text{closed}} V_{DK}^{EK} + f\sum_V^{\text{open}} V_{DV}^{EV}, \quad (25c)$$

$$F_L^T = F_L^D = F_T^D = 0. \quad (25d)$$

Labels L, M, and K refer to closed shell spinors, U, T, and V refer to open shell spinors, and D, E, and F refer to virtual spinors. The open shell spinors have a fractional occupation f $(0<f<1)$ and a is a coupling constant $m(n-1)/n(m-1)$ with m the number of open shell spinors and n the number of open shell electrons. This formalism becomes Kramers-restricted if we apply the constraint that the two components of a Kramers pair always belong to the same space (closed, open or virtual).

In this scheme the spinors are uniquely defined, provided that there are no degeneracies among spinors with the same

symmetry character. Different choices of the open and closed shell subspaces do, however, influence the form of the spinors and hence of the zeroth order Hamiltonian. In the sample calculation section we consider different ways of calculating of the spin–orbit splitting of the ClO molecule and of the chlorine atom to assess the sensitivity of the method to a particular SCF scheme and hence to a different choice of spinors.

III. POINT GROUP SYMMETRY

In the formulas given above we did not yet consider use of point group symmetry. This can be done using double group theory via the so-called group-chain method.[36] The group-chain method considers only the highest Abelian subgroups of the full symmetry group at the CCSD(T) level, while it takes full point group symmetry into account up to the molecular integral transformation step. The advantage of this method is that the formulas remain simple, while it still takes some account of speed-ups due to higher point group symmetry by creating real-valued integrals instead of the generally complex-valued integrals.

We have spinors that are symmetry functions of the highest Abelian double point group of the molecule. These spinors are labeled by the irreducible representation (irrep) γ of the point group with an index p running over functions within this irrep. This labeling makes it possible to discard matrix elements that are zero due to symmetry. 1-electron matrix elements are only nonzero when both spinors are in the same Abelian irrep γ. 2-electron matrix elements are nonzero when the direct product of the four irreps involved is the totally symmetric irrep. Since the double groups have complex valued irreps it is of importance whether a spinor is used as a bra- or ket-function when calculating this direct product.

Consider for example the point group C_4. This double group has four ''fermion'' irreps ${}'E_1$, ${}''E_1$, ${}'E_2$, and ${}''E_2$ and four ''boson'' irreps a, b, $'e$, and $''e$. The integral $\langle {}'E_1\,{}''E_2 | {}'E_1\,{}''E_2\rangle$ belongs to irrep $({}'E_1\otimes{}''E_2)^*\otimes({}'E_1\otimes{}''E_2)=b^*\otimes b=b\otimes b=a$. It is therefore in general nonzero. If we permute indices 2 and 3 we have the integral $\langle {}'E_1\,{}'E_1 | {}''E_2\,{}''E_2\rangle$, which belongs to irrep $({}'E_1\otimes{}'E_1)^*\otimes({}''E_2\otimes{}''E_2)={}'e^*\otimes{}''e={}''e\otimes{}''e=b$. This integral is always zero.

We can now rewrite our equations in symmetry-reduced form.[37] For brevity we will not repeat all equations in this form but give some representative examples. The energy expression becomes

$$E^{\mathrm{CCSD}}=\sum_{\gamma}\sum_{i,a} F_a^i(\gamma)T_i^a(\gamma) + \sum_{\gamma}\sum_{\gamma_j}\sum_{\gamma_b}\sum_{ij,ab} V_{ab}^{ij}(\gamma_b,\gamma_j,\gamma)T_{ij}^{ab}(\gamma_b,\gamma_j,\gamma). \tag{26}$$

In the second term we only need to sum over γ_j and γ_b, since γ_i and γ_a are fixed by the constraints $\gamma_i\otimes\gamma_j=\gamma$ and $\gamma_a\otimes\gamma_b=\gamma$. For the same reason we omit the redundant labels γ_i and γ_a in the matrices V and T. The third term in the update of T_1 [Eq. (4)] is written as

$$T_i^a(\gamma)=\sum_c H_c^a(\gamma)T_i^c(\gamma). \tag{27}$$

The fourth term in the update of T_2 [Eq. (5)] is written as

$$T_{ij}^{ab}(\gamma_b,\gamma_j,\gamma)=\sum_{\gamma_i}\sum_{kl} A_{ij}^{kl}(\gamma_j,\gamma_l,\gamma)\tau_{kl}^{ab}(\gamma_l,\gamma_b,\gamma). \tag{28}$$

For the 4-index arrays different symmetry-orderings are possible. For the update in Eq. (28) it is most convenient to combine both the i and j and the k and l indices into the compound indices ij and kl. For other terms other orderings of the arrays are preferable. For instance in the evaluation of the last term in the T_1 update [Eq. (4)] we write

$$T_i^a(\gamma)=\sum_{\gamma_{ckl}}\sum_{kl,c} V_{ic}^{kl}(\gamma,\gamma_{ckl},\gamma)\tau_{kl}^{ac}(\gamma_{ckl},\gamma,\gamma). \tag{29}$$

In this case γ_i and γ_a are equal to γ.

In general we can distinguish four different types of ordering in the 4-index arrays, symbolically written as (3:1) or (γ_{pqr},γ_s), (1:3) or (γ_p,γ_{qrs}), $(2{:}2)_1$ or $(\gamma_{pq},\gamma_{rs})$ and $(2{:}2)_2$ or $(\gamma_{pr},\gamma_{qs})$. A block γ_{pqr} is hereby further subdivided either as (γ_{pq},γ_r) or as (γ_p,γ_{qr}). For the two-index compound indices one can often use triangular indices $pq(p>q)$ because of the permutation symmetry $X_{PQRS}=-X_{QPRS}$ that most of the intermediate arrays possess.

IV. IMPLEMENTATION

The algorithm sketched above has been implemented in the FORTRAN code RELCCSD. Prerequisites are a list of integrals over molecular 4-spinors and the multiplication table of the Abelian double group of the system.

Integrals are symmetry-packed and sorted into the six types ($\langle oo\|oo\rangle$, $\langle vo\|oo\rangle$, $\langle vv\|oo\rangle$, $\langle vo\|vo\rangle$, $\langle vv\|vo\rangle$ and $\langle vv\|vv\rangle$ with o=occupied, v=virtual) before the iterative process is started. This is at present done using a built-in interface to the MOLFDIR integral transformation codes which gives a Kramers-unique list of integrals. The $\langle vv\|vv\rangle$ array is in general too large to fit in central memory. The T_2 update that involves this class of integral is therefore written to work with fixed-size batches of integrals. The same is done in the CCSD step with the contributions from the second-largest class, the $\langle vv\|vo\rangle$ integrals. The final minimal memory requirements of the CCSD step are of the order of six times the T_2 amplitude vector and of four times this vector plus the length of the $\langle vv\|vo\rangle$ array in the CCSD(T) step.

As standard order, according to which the integrals are stored on disk, we have chosen $(2{:}2)_1$. Terms that are more efficiently evaluated in other orderings are treated using an in-core sort before and after the actual matrix-multiplication. Since these sorts are of order n^4 at most, they are of vanishing importance in the cpu-performance of the program when the system treated becomes larger.

TABLE I. Total energies (hartrees) and fine structure splitting (FSS, cm^{-1}) of the $^2\Pi$ ground state of ClO. The ClO bond length used is 2.9662 a_0 (Ref. 46).

	2 sets of spinors (scheme a)			1 set of spinors (scheme b)		
Method	E ($^2\Pi_{1/2}$)	E ($^2\Pi_{3/2}$)	FSS	E ($^2\Pi_{1/2}$)	E ($^2\Pi_{3/2}$)	FSS
Reference	−535.683 377	−535.684 403	−225.2	−535.682 425	−535.683 454	−225.9
CCSD	−536.115 396	−536.116 775	−302.6	−536.115 305	−536.116 688	−303.5
CCSD+T	−536.136 619	−536.138 061	−316.4	−536.138 095	−536.136 644	−318.5
CCSD(T)	−536.134 477	−536.135 902	−312.6	−536.134 516	−536.135 939	−312.4
CCSD-T	−536.134 337	−536.135 770	−314.5	−536.134 401	−536.135 838	−315.3
Expt.[a]			−318			−318

[a]Reference 46.

The crucial steps in the algorithm are the evaluations of formulas (9)–(16) and (18), (20), and (21). We have implemented these using the BLAS routines XGEMM, XGEMV, XAXPY, and XDOT with X=S, D, C, or G for single/double precision and real/complex arithmetic. In the FORTRAN code we use no explicit real or complex arithmetic but pass pointers to arrays that may contain either real or complex data. Only when the routines XGEMM, etc. are called the distinction between complex/real single/double precision is made and the appropriate BLAS routine is called. At the higher level we only need to calculate the correct sizes of the arrays in terms of 8-byte real words. This present implementation makes it possible to run the same source code on 32 and 64 bit machines and use complex or real arithmetic depending on the appropriate double point group.

Some machine-specific code was written to increase the performance on CRAY-J932 and C90 computers. This version of the code uses dynamical allocation of memory and reduces I/O by keeping integrals in core memory when possible.

V. SAMPLE CALCULATIONS

We present some calculations based on the Dirac–Coulomb–Gaunt Hamiltonian to illustrate the use of the formalism derived above. This Hamiltonian includes all terms to order α^2 which contribute to the spin–orbit splitting, i.e., in terms of the Breit–Pauli Hamiltonian, the spin-own-orbit and spin-other-orbit terms are included as well as all the spin–spin terms. The inclusion of these terms has been found necessary to obtain quantitative predictions of spin–orbit splittings for light atoms. The basis sets employed were based on the aug-cc-pVTZ sets from Dunning and co-workers,[38–40] extended and recontracted to account for the relativistic change in the orbitals.[41,42] The relativistic contraction coefficients for the oxygen basis set were not published previously and are obtained using a modified version[43] of GRASP.[44] To describe the relativistic contraction of the $2p_{1/2}$ spinor of oxygen one extra tight p-function with exponent 196.388 225 0 was added before recontracting Dunning's basis.

A. ClO

The ClO radical is an example of a molecule with a spin–orbit split ground state. Since the spin–orbit splitting in chlorine is considerably larger than in oxygen it is of importance where the open shell electron is mainly located. The accuracy with which this location is determined will depend on how well the method used describes the electron affinities of the constituent atoms, and since these are poorly described at the SCF level of theory, we expect electron correlation to be important for the calculation of the fine-structure-splitting in ClO.

To study the influence of the choice of SCF procedure we use two schemes to generate the spinors. In scheme a we use different sets of spinors for the two components of the $^2\Pi$ ground state. We generate spinors for the $^2\Pi_{3/2}$ state by including the $\pi^*_{1/2}$ spinors in the closed shell space and giving the $\pi^*_{3/2}$ spinors a fractional occupation of 1/2. In the

TABLE II. Total energies (hartrees) and fine structure splittings (FSS, cm^{-1}) of the ^2P state of the chlorine atom. Cl is treated as a 7 valence electron atom.

	2 sets of spinors (scheme a)			1 set of spinors (scheme b)		
	E ($^2P_{1/2}$)	E ($^2P_{3/2}$)	FSS	E ($^2P_{1/2}$)	E ($^2P_{3/2}$)	FSS
Reference	−460.813 946	−460.817 928	−873.7	−460.813 862	−460.817 912	−888.9
CCSD	−461.005 285	−461.008 986	−812.3	−461.005 173	−461.008 937	−826.1
CCSD+T	−461.011 536	−461.015 456	−860.4	−461.011 416	−461.015 405	−875.6
CCSD(T)	−461.011 596	−461.015 453	−846.6	−461.011 477	−461.015 403	−861.5
CCSD-T	−461.011 601	−461.015 453	−845.4	−461.011 483	−461.015 403	−860.3
Expt.[a]			−882.4			−882.4

[a]Reference 47.

TABLE III. Total energies (hartrees) and fine structure splittings (FSS, cm^{-1}) of the ^2P state of the chlorine atom. Cl is treated as a 5 valence electron atom.

	2 sets of spinors (scheme a)			1 set of spinors (scheme b)		
	$E\ (^2P_{1/2})$	$E\ (^2P_{3/2})$	FSS	$E\ (^2P_{1/2})$	$E\ (^2P_{3/2})$	FSS
Reference	−460.813 946	−460.817 928	−873.7	−460.813 862	−460.817 912	−888.9
CCSD	−460.925 752	−460.929 763	−880.4	−460.925 658	−460.929 723	−892.1
CCSD+T	−460.929 423	−460.933 415	−876.3	−460.929 322	−460.933 373	−889.0
CCSD(T)	−460.929 418	−460.933 410	−876.1	−460.929 319	−460.933 368	−888.6
CCSD-T	−460.929 421	−460.933 413	−876.1	−460.929 323	−460.933 370	−888.7
Expt.[a]			−882.4			−882.4

[a]Reference 47.

same fashion we generate a set of spinors for the $^2\Pi_{1/2}$ state by making the opposite choice; we include the $\pi^*_{3/2}$ in the closed shell space and place the $\pi^*_{1/2}$ in the open shell. In scheme b we generate a common set of spinors for both states by including both $\pi^*_{1/2}$ and the $\pi^*_{3/2}$ spinors in the open shell space with a fractional occupation of 3/4.

The $1s$-spinors of O and the $1s$, $2s$, $2p$ spinors of Cl were frozen after the SCF step, giving an active space of 13 electrons in the correlation calculation. The results for both schemes are given in Table I.

From the results in Table I it is evident that a SCF treatment alone is insufficient to obtain a reliable fine-structure-splitting for this molecule, and even the CCSD treatment falls short of experiment by 15 cm^{-1}. We also see that the particular choice of SCF occupation is not very important for the CCSD result. The most complete level of theory, the CCSD-T level, yields a fine-structure-splitting that is 3 cm^{-1} smaller than the experimental value of -318 cm^{-1}.

We can compare with the previous theoretical work by Koseki, Schmidt, and Gordon.[45] They used effective one-electron one-center spin–orbit operators that were calibrated against known fine-structure-splittings. They find -255.65 cm^{-1} using the MCSCF/6-31G(d,p) method and -258.96 cm^{-1} with the MCSCF/MC-311G(d,p) method. This rather large discrepancy with the experimental value may be due to either the limited electron correlation included in the MCSCF method or the one-electron one-center approximations.

B. Cl atom

For the Cl atom we again test the influence of the SCF-procedure on the results. We have 5 $3p$ electrons that give rise to a spin–orbit split ^2P ground state. The spinors are split into a set of two $3p_{1/2}$ spinors and a set of four $3p_{3/2}$ spinors. In scheme a, where we use two sets of spinors, we generate spinors for the $^2P_{3/2}$ state by including the $3p_{1/2}$ spinors in the closed shell space and giving the $3p_{3/2}$ spinors a fractional occupation of 3/4. In the same way we generate spinors for the $^2P_{1/2}$ state by making the opposite choice; we include the $3p_{3/2}$ in the closed shell space and give the open shell $3p_{1/2}$ spinors a fractional occupation of 1/2. In scheme b we generate a common set of spinors for both states by including both $3p_{1/2}$ and the $3p_{3/2}$ spinors in the open shell space and giving them a fractional occupation of 5/6. The $1s$,$2s$,$2p$ spinors of Cl were frozen after the SCF step, giving an active space of 7 electrons in the correlation calculation. The results for both schemes are given in Table II.

We see that the particular choice of SCF occupation now influences the result significantly. It is also clear that although the reference FSS value is close to the experimental value, correlation effects are large. Inclusion of only single and double excitations as is done in the CCSD model is insufficient in this case. Higher order corrections are very important and their omission results in significant errors in the splitting. The most important correlating configurations come from a single excitation from the $3s$ into the $3d$ shell with recoupling of the $3p$ electrons, which is partly balanced by the triple excitation term. In Cl we can isolate the effect of this $3s-3d$ excitation by freezing the $3s$ electrons and treating the atom as a 5 valence electron system (Table III). This reduces the effect of correlation dramatically. In this case the difference between schemes a and b is also much smaller. The large effect of higher order excitations is not as apparent in ClO, because the recoupling of the $3p$ shell is no longer possible due to the molecular environment.

This illustrates the limitations of the method. Results may vary slightly according to the choice of spinor generation method. In cases where the spin–orbit splitting is rela-

TABLE IV. Total energies (hartrees) and fine structure splitting (FSS, cm^{-1}) of the $^2\Pi_g$ ground state of O_2^-. The O–O distance used is 2.5511 a_0.

	Reference	CCSD	CCSD(T)	CCSD-T
$E\ (^2\Pi_{1/2})$	−149.727 333	−150.228 232	−150.252 157	−150.251 569
$E\ (^2\Pi_{3/2})$	−149.728 167	−150.228 965	−150.252 874	−150.252 286
FSS	−183.0	−161.0	−157.4	−157.5

TABLE V. Total energies (hartrees) and fine structure splitting (FSS, cm^{-1}) of the $^2\Pi_g$ ground state of O_2^+. The O–O distance used is 2.1097 a_0.

	Reference	CCSD	CCSD(T)	CCSD-T
$E\ (^2\Pi_{1/2})$	−149.315 097	−149.775 451	−149.798 452	−149.797 866
$E\ (^2\Pi_{3/2})$	−149.314 086	−149.774 538	−149.797 552	−149.796 965
FSS	221.8	200.4	197.6	197.7

TABLE VI. Total energies (hartrees) and fine structure splitting (FSS, cm^{-1}) of the $^2\Pi$ ground state of FO. The FO bond length used is 2.5058 a_0 (Ref. 45).

	Reference	CCSD	CCSD(T)	CCSD-T
E ($^2\Pi_{1/2}$)	−174.319 628	−174.798 392	−174.816 172	−174.815 499
E ($^2\Pi_{3/2}$)	−174.320 471	−174.799 271	−174.817 057	−174.816 385
FSS	−184.9	−192.9	−194.4	−194.6

tively small, the best choice appears to use one set of spinors for the different spin–orbit components, as has been found in numerical atomic calculations. This is computationally favourable, since one needs only one SCF calculation and 4-index transformation. The reference splitting is also usually somewhat better due to the more balanced treatment of the different components. We will use scheme b for the next set of calculations on O_2^+, O_2^-, and FO.

C. O_2^+ and O_2^-

The positive and negative ions of the oxygen molecule have a spin–orbit split $^2\Pi$ ground state. We did the same type of calculations as described above for ClO with a valence space of 11 active electrons and 13 active electrons for O_2^+ and O_2^-, respectively. The results are given in Tables IV and V.

The CCSD(T) and CCSD-T values are both in good agreement with the experimental value of -160 cm^{-1} for O_2^- and 197.3 cm^{-1} for O_2^+. Electron correlation in both cases reduces the splitting.

D. FO

The FO molecule has the same valence electron configuration as ClO. Taking the average of the CCSD(T) and CCSD-T values and rounding to the nearest whole number, we calculate the FSS for FO to be -195 cm^{-1}. Since the CCSD-T result should have a similar accuracy as found for the calculations on ClO and O_2^- and also because the correlation contribution is considerably smaller for FO relative to ClO and O_2^-, we believe that this will be accurate to ± 4 cm^{-1} (see Table VI). The experimental value[48] of $-193.80(97)$ confirms the accuracy of the method.

We can compare with previous theoretical work by Koseki, Schmidt, and Gordon,[45] who used effective one-electron one-center spin–orbit operators that were calibrated against known fine-structure-splittings. They find -187.90 cm^{-1} using the MCSCF/6-31G(d,p) method, which is in reasonable agreement with our best value of -195 cm^{-1}. Their approximate scheme usually gives results that are within 20% of the experimental value, which is consistent with our findings.

It is interesting to note that for all the molecules studied, the effect of the triples correction on the FSS was a shift in the same direction as the CCSD correlation correction, but for the Cl atom the corrections were in opposite directions. The special nature of the atomic correlation problem in the Cl atom that affects the triples correction has been pointed out already.

VI. CONCLUSIONS

An unrestricted coupled-cluster formalism is presented for use in relativistic spin-dependent molecular calculations. The method has been implemented and interfaced to the MOLFDIR program system. Double group theory is used to reduce computational requirements. The present implementation makes it possible to perform CCSD(T) calculations for molecular systems using the full 4-component Dirac–Coulomb–Gaunt Hamiltonian. This provides a scheme in which the accuracy is mainly dependent on the quality and size of the basis sets that can be used instead of on the approximations made in the treatment of relativity.

The predicted fine structure splittings in Cl, ClO, FO, O_2^+, and O_2^- are within a few wave numbers from the experimental values. This gives confidence that this method may give reliable predictions of the fine structure splittings of similar compounds for which experimental data are not available.

ACKNOWLEDGMENTS

L.V. was supported by a National Research Council postdoctoral fellowship and a Cray Research Grant. K.G.D. was supported by a prime Contract No. NAS2-14031 from NASA to Eloret and by Contract No. BPNL 291140-A-A3 from Pacific Northwest Laboratory to Eloret. Pacific Northwest Laboratory is a multiprogram laboratory operated by the Batelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76RLO-1830; the work was performed under the auspices of the Office of Scientific Computing and under the Office of Health and Environmental Research, which funds the Environmental and Molecular Sciences Laboratory Project, D-384.

[1] J. Cizek, Adv. Chem. Phys. **14**, 35 (1969).
[2] J. Cizek and J. Paldus, Int. J. Quantum Chem. Symp. **5**, 359 (1971).
[3] G. D. Purvis III and R. J. Bartlett, J. Chem. Phys. **76**, 1910 (1982).
[4] R. J. Bartlett, J. Phys. Chem. **93**, 1697 (1989).
[5] J. Paldus, in *Relativistic and Electron Correlation Effects in Molecules and Solids*, edited by G. L. Malli (Plenum, New York, 1994), Vol. 318, p. 207.
[6] L. L. Foldy and S. A. Wouthuysen, Phys. Rev. **78**, 29 (1950).
[7] M. Douglas and N. M. Kroll, Ann. Phys. (NY) **82**, 89 (1974).
[8] K. G. Dyall, J. Chem. Phys. **100**, 2118 (1994).
[9] C. Chang, M. Pélissier, and P. Durand, Phys. Scr. **34**, 394 (1986).
[10] J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist, and M. Mårtensson-Pendrill, J. Phys. B **19**, 2799 (1986).
[11] E. Van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
[12] W. C. Ermler, Y. S. Lee, P. A. Christiansen, and K. S. Pitzer, Chem. Phys. Lett. **81**, 70 (1981).
[13] R. M. Pitzer and N. W. Winter, J. Phys. Chem. **92**, 3061 (1988).
[14] C. M. Marian, in *New Challenges in Computational Quantum Chemistry*, edited by P. J. C. Aerts, P. S. Bagus, and R. Broer (The University of Groningen, Groningen, 1994), p. 145.
[15] M. M. Gleichmann and B. A. Hess, J. Chem. Phys. **101**, 9691 (1994).
[16] E. Ilyabaev and U. Kaldor, Phys. Rev. A **47**, 137 (1993).
[17] E. Ilyabaev and U. Kaldor, J. Chem. Phys. **97**, 8455 (1992).

[18] L. Visscher, K. G. Dyall, and T. J. Lee, Int. J. Quantum Chem. Symp. **29**, 411 (1995).
[19] D. Jayatilaka and T. J. Lee, Chem. Phys. Lett. **199**, 211 (1992).
[20] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[21] K. Raghavachari, Annu. Rev. Phys. Chem. **42**, 615 (1991).
[22] T. J. Lee and G. Scuseria, in *Quantum Mechanical Electronic Structure Calculations with Chemical Accuracy*, edited by S. R. Langhoff (Kluwer Academic, Dordrecht, 1995), pp. 47–108.
[23] M. J. O. Deegan and P. J. Knowles, Chem. Phys. Lett. **227**, 321 (1994).
[24] M. Urban, J. Noga, S. J. Cole, and R. J. Bartlett, J. Chem. Phys. **83**, 4041 (1985).
[25] T. J. Lee, A. P. Rendell, K. G. Dyall, and D. Jayatilaka, J. Chem. Phys. **100**, 7400 (1994).
[26] C. Murray and E. R. Davidson, Int. J. Quantum Chem. **43**, 755 (1992).
[27] C. Murray and N. C. Handy, J. Chem. Phys. **97**, 6509 (1992).
[28] P. J. Knowles, J. S. Andrews, R. D. Amos, N. C. Handy, and J. A. Pople, Chem. Phys. Lett. **186**, 130 (1991).
[29] T. D. Crawford, H. F. Schaefer, and T. J. Lee, J. Chem. Phys. **105**, 1060 (1996).
[30] P. Neogrády and M. Urban, Int. J. Quantum Chem. **55**, 187 (1995).
[31] T. D. Crawford and H. F. Schaefer, J. Chem. Phys. **104**, 6259 (1996).
[32] D. Jayatilaka and T. J. Lee, J. Chem. Phys. **98**, 9734 (1993).
[33] L. Visscher, O. Visser, P. J. C. Aerts, H. Merenga, and W. C. Nieuwpoort, Comp. Phys. Commun. **81**, 120 (1994).
[34] C. C. J. Roothaan, Rev. Mod. Phys. **32**, 179 (1960).
[35] O. Visser, L. Visscher, P. J. C. Aerts, and W. C. Nieuwpoort, J. Chem. Phys. **96**, 2910 (1992).
[36] L. Visscher, Chem. Phys. Lett. **253**, 20 (1996).
[37] T. J. Lee and J. E. Rice, Chem. Phys. Lett. **150**, 406 (1988).
[38] T. H. Dunning Jr., J. Chem. Phys. **90**, 1007 (1989).
[39] D. Woon and T. Dunning Jr., J. Chem. Phys. **98**, 1358 (1993).
[40] R. A. Kendall, T. H. Dunning Jr., and R. J. Harrison, J. Chem. Phys. **96**, 6796 (1992).
[41] L. Visscher and K. G. Dyall, J. Chem. Phys. **104**, 9040 (1996).
[42] L. Visscher, J. Styszyñski, and W. C. Nieuwpoort, J. Chem. Phys. **105**, 1987 (1996).
[43] K. G. Dyall and K. Faegri, Jr., Theor. Chim. Acta **94**, 39 (1996). Some additional modifications were made by T. Saue and L. Visscher to interface the code to the MOLFDIR program system.
[44] K. G. Dyall, I. P. Grant, C. T. Johnson, E. P. Plummer, and F. Parpia, Comp. Phys. Commun. **55**, 425 (1989).
[45] S. Koseki, M. W. Schmidt, and M. S. Gordon, J. Phys. Chem. **96**, 10 768 (1992).
[46] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
[47] C. E. Moore, *Atomic Energy Levels (H-V)* (National Bureau of Standards, Washington, D.C., 1949).
[48] P. D. Hammer, A. Sinha, J. B. Burkholder, and C. J. Howard, J. Mol. Spectrosc. **129**, 99 (1988).